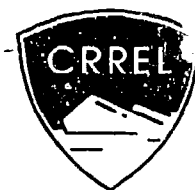


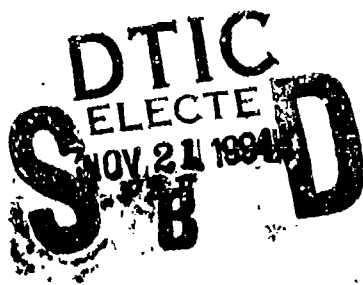
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Screening for Metals by X-Ray Fluorescence Spectrometry Using a Single Calibration Standard

Alan D. Hewitt

July 1994



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Abstract

Analysis for copper, zinc, arsenic and lead was performed on a variety of solid particle matrices using a portable, high-resolution X-ray fluorescence (XRF) spectrometer. All quantitative determinations were based on an instrumental calibration method that uses a single certified reference material to establish elemental response factors and the Compton K_{α} peak to normalize for matrix discrepancies. This simple approach to XRF analysis circumvents the need to acquire matrix matched standards for either empirical coefficients or fundamental parameter methods of calibration. Preliminary results show that response factor/Compton K_{α} peak normalization is a promising approach when screening for these metals in soils, dust, paint chips and incinerated sludge.

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**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

Funding for this work was provided by the U.S. Army Environmental Center, Martin Stutz, Project Monitor. The author thanks Dr. I. M. Spittler for suggesting the response factor / Compton K_{α} peak normalization method of analysis and James Cragin and Dr. Clarence L. Grant for critical reviews of the text.

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Screening for Metals by X-Ray Fluorescence Spectrometry Using a Single Calibration Standard

ALAN D. HEWITT

INTRODUCTION

Both natural and anthropogenic levels of metals in soil are of human health concern. X-ray fluorescence (XRF) spectrometry is a nondestructive method of total metal analysis that requires very little sample preparation. For this reason XRF is an efficient and cost-effective means of identifying and quantifying pollutant metals in solid materials during remedial investigations and feasibility studies (RI/FS) for hazardous waste site investigations. Moreover, on-site screening for pollutant metals with XRF has received the approval of the U.S. Environmental Protection Agency (EPA 1987). The data quality specification often recommended for field screening by XRF analysis is a precision of $\pm 10\%$, an accuracy of $\pm 50\%$ and detection limits of less than 1000 parts per million (Raab et al. 1987). The main objective during field screening exercises is to quickly locate and delineate the areas of heaviest contamination. Several studies have demonstrated XRF's ability to satisfy these criteria by using either laboratory-based (Frust et al. 1985, Grupp et al. 1989, Watson et al. 1989, Harding 1991) or field-portable instruments (Piorek and Rhodes 1988, Ash et al. 1991, Carlson and Alexander 1991, Driscoll et al. 1991, Garby 1991).

In the past most of the field-portable XRF site screening was performed with systems equipped with gas proportional detectors. This type of detector has a spectral resolution of about 1000 electronvolts (eV), restricting its suitability to cases where a single metal was being determined or where the metals of interest have well-resolved X-ray fluorescence peaks. Recently a new generation of field-portable XRF systems have become available (Ash et al. 1991, Driscoll et al. 1991). They are equipped with silicon (drifted with lithium) [Si(Li)] or mercuric iodide (HgI_2) detectors with resolutions of 170 and 300 eV, respectively. These field-transportable, high-resolution systems can provide unambiguous qualitative identification of

more complex mixtures of metals in environmental samples by generating the same unique metal spectra as the more expensive laboratory-based systems. The major difference between field and laboratory instruments is that the former have a sealed radioisotope as the primary radiation source. These sources are smaller and less energetic, so the portable instruments are not as sensitive as most laboratory-based systems. The selection and number of sources that can be installed in a field-portable XRF instrument control the range of elements that can be detected. This combination of sealed primary sources, along with a detector requiring a liter or less of liquid nitrogen, microprocessors and rechargeable battery packs, has allowed for the construction of rugged, compact and lightweight instruments capable of several hours of remote operation (manufactured by HNU Systems Inc., Spectrace Instruments Inc. and Outokumpu Electronics).

Today the manufacturers of these field-portable, high-resolution XRF systems are focusing their attention on the user friendliness and the robustness of applications for environmental sample analysis. Applications that are insensitive to sample matrices are necessary in order to limit the number of calibration standards required to handle the diverse range of samples that can be encountered during a hazardous waste site investigation (e.g. soil composition, sludge, dust, paint chips, etc.).

Two of the field-portable XRF instruments currently being marketed are capable of analyses based on empirical calibration coefficients, which requires the entry of several site-specific or generic matrix standards (HNU Systems Inc. and Outokumpu Electronics). The HNU instrument also has a Compton peak normalization analysis method. The other manufacturer (Spectrace Instruments, Inc.) offers only a fundamental parameters analysis method for environmental samples. The major advantage of using fundamental parameters for quantitative metal evaluations is that

the sample analysis is not delayed by having to either establish site-specific standards or enter multiple calibration points for each sample matrix or both.

Until robust (matrix-insensitive) fundamental parameter applications are universal, Spittler* has proposed that the accuracy necessary for a preliminary site investigation, for many of the more frequently encountered metal pollutants such as lead (Pb), arsenic (As) and zinc (Zn), could be achieved by a single-point instrumental calibration method that includes a matrix normalization parameter. This method requires only a single certified reference material containing the analytes of interest in a matrix that is physically consistent with the samples (particles), plus normalization of the incoherent radiation backscattering. Incoherent radiation backscatter is caused by the light elements and the analyte concentration in the sample matrix. Traditionally the ratio of the incoherent (Compton) and coherent (Rayleigh) backscatter has been used for matrix correction with environmental samples (Nielson and Sander, 1983, Christensen and Drabaek 1986, Rachetti and Wegscheider 1986). However, to fulfill the objec-

tive of field screening, only the intensity of the former peak is necessary.

In this study I evaluated the utility of environmental sample analysis based on a single certified standard and normalization for the incoherent backscattering. This preliminary effort covered the quantification of copper (Cu), Zn, As and Pb in a wide variety of solid particle matrices.

XRF ANALYSIS

The detection of metals by XRF analysis is the result of the emission of element-specific energies (photons) that occurs when an electron from an outer orbital loses energy in order to fill a void in an inner shell. This emitted energy is called X-ray fluorescence and is measured in kiloelectronvolts (keV; 1 keV = 1000 eV). The electron vacancy in the inner shell (the nonvalence shell) is created by exposure to a beam of gamma or X-ray energy that is close to and above its excitation energy (Fig. 1). The probability for an electron to become excited and ejected from a shell increases with a decreasing difference between incident and excitation energy levels. For example, the incident energies (two levels) coming from the primary cadmium-109 (^{109}Cd) X-ray source are 21.16 and 22.99 keV, which are more likely to cause electrons to be lost

*Personal communication, L.M. Spittler, U.S. EPA, Environmental Services Division, Region I, Lexington, Massachusetts, 1989.

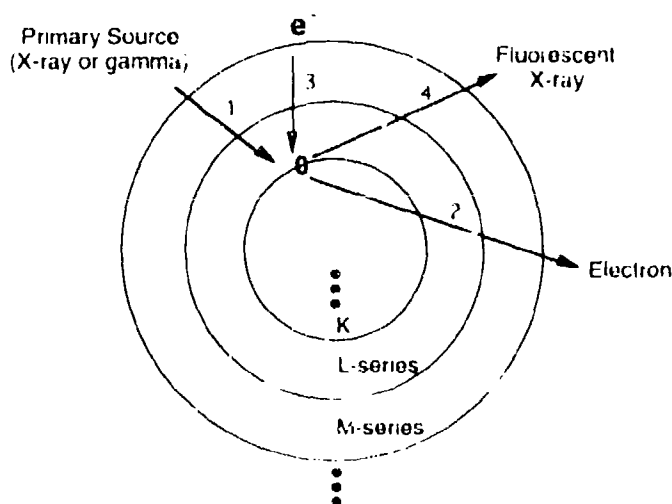


Figure 1. Process of X-ray fluorescence. The numbers indicate the order of events.

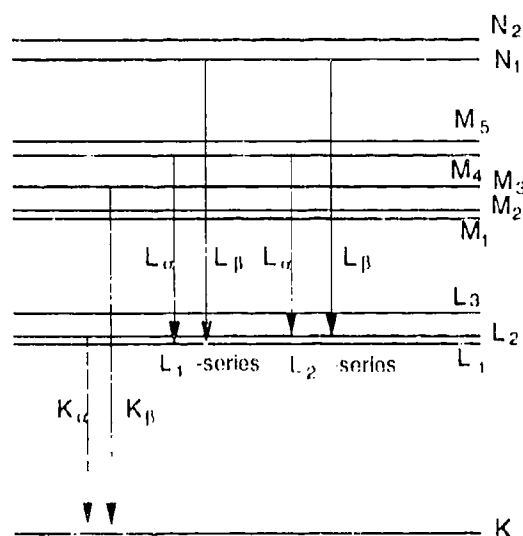


Figure 2. K_{α} , K_{β} , L_{α} and L_{β} X rays.

from the K shell of selenium (Se), with an excitation energy level of 12.66 keV, than from Cr, with a corresponding excitation energy level of 5.989 keV.

Of the metals detectable by XRF analysis, the K and L electron shells are the ones most frequently

filled. These two letters, along with α , β and γ subscripts denoting the outer shells from which the electrons fell (Fig. 2), serve as the nomenclature for the discrete spectral energies measured. Moreover, since there is more than one atomic energy level (shell) from which an electron can fall, there are always at least two emission energies for each element (Fig. 2). For this reason the spectral energies of greatest interest for the analysis of pollutant metals are the K_{α} , K_{β} or the L_{α} , L_{β} spectral lines (Table 1).

Probability also comes into play for the electrons filling the void created. The spectral intensity ratios of the α and β emission peaks is 7:1 when a K shell is filled and 9:6 for the L shells. It is much easier to observe these emission peak ratios with a high-resolution XRF spectrometer, thus aiding in the identification of a sample's elemental composition. Furthermore, since a high-resolution XRF can resolve all these α and β peaks, it allows for the selection of a secondary peak for quantitative analysis when the energies of two emission peaks from different elements overlap.

Figure 3 is an example of the spectrum obtained with a high-resolution portable XRF system. This analysis was performed on an aqueous solution containing 1000 mg/L each of Cr, nickel (Ni), Cu, Zn, As and Se. The intensities of each characteristic K_{α} peak increases for the same analyte concentration because discrete elemental excitation energies are successively closer to the incident energy generated by the ^{109}Cd radioactive source. In addition, the 7:1 intensity ratio between K_{α} and K_{β} peaks can be seen for Zn, As and Se.

Table 1. Primary sources and analyte lines for metals of environmental concern that can be detected by XRF spectrometry.

| Emission lines (keV) | | | | |
|--------------------------------|--------------|-------------|--------------|-------------|
| Metals | K_{α} | K_{β} | L_{α} | L_{β} |
| ^{109}Cd X-ray source | | | | |
| Cr | 5.41 | 5.95 | | |
| Mn | 5.89 | 6.49 | | |
| Fe | 6.40 | 7.06 | | |
| Co | 6.92 | 7.65 | | |
| Ni | 7.47 | 8.30 | | |
| Cu | 8.04 | 8.94 | | |
| Zn | 8.63 | 9.61 | | |
| As | 10.5 | 11.5 | | |
| Se | 11.2 | 12.6 | | |
| Hg | | | 9.98 | 11.9 |
| Pb | | | 10.3 | 12.3 |
| | | | 10.5 | 12.6 |
| ^{241}Am X-ray source | | | | |
| Ag | 23.1 | 25.2 | | |
| Cd | 23.1 | 26.4 | | |
| Sn | 25.2 | 28.8 | | |
| Sb | 26.2 | 30.1 | | |
| Ba | 32.0 | 36.8 | | |

INSTRUMENTATION

The instrument used in this study was the X Met 920 (Outokumpu Electronics) X-ray spectrophotometer. This system is equipped with a Si(Li) energy dispersive detector, a surface analysis probe and ^{109}Cd and americium 241 (^{241}Am) primary radioactive sources. The combination of these two primary sources allows for the estimation of all the metals listed in Table 1. The Si(Li) semiconductor detector has a resolution of 170 eV and is cooled by a 0.5 L liquid nitrogen reservoir. A preamplified signal is sent from this detector to a multi-channel analyzer (MCA), which separates the energy spectrum into 2048 channels. These channels correspond to spectral energies (keV), and the number of counts stored in each channel indicates signal intensity. The MCA is housed in a computer, the

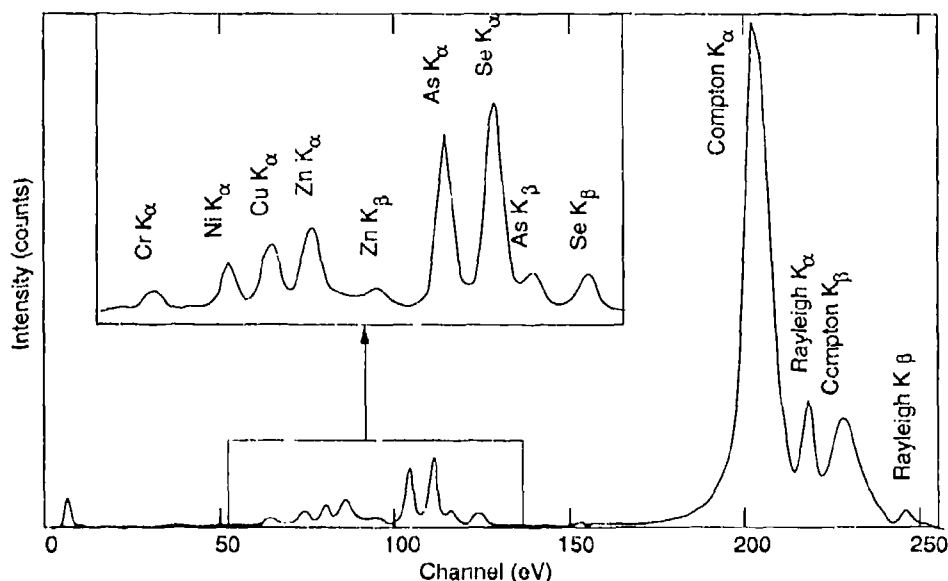


Figure 3. Spectrum of a solution containing 1000 mg/L of Cr, Ni, Cu, Zn, As and Se.

selection of which allows the system to either be capable of eight hours of battery-pack-powered, in-situ analysis or continuous, AC-powered, on-site analysis.

Figure 3 is an example of a 256-channel spectral output. All of the major emission peaks of these elements are well resolved, allowing for rapid elemental identification. In comparison, gas proportional detectors, with a resolution of around 1000 eV, would not be capable of resolving the Ni, Cu and Zn emission peaks or the As and Se peaks shown in Figure 3 (Table 1).

The X-Met 920 system was configured for on-site analysis of bulk samples held in either 31- or 40 mm diameter cups. Field samples collected for on-site analysis are often dried and sieved prior to analysis. Several studies have found that these two operations can be performed in less than a couple of hours, making it possible to analyze tens to a hundred samples in a single day (Crupe et al. 1989, Gabry 1991). The bulk of the particles in the samples analyzed during this study would pass through a 30-mesh sieve, thus having an average size of <600 μm .

CALIBRATION

Ideally a calibrated XRF system establishes the total metal concentration in the portion of the sample that is irradiated during analysis. If the

sample medium is homogeneous, then this concentration estimate corresponds to the entire sample retained in the cup. Direct measurement of the intensities of the various discrete spectral energies for quantitative interpretation, however, is often confounded by other elements present in the sample due to absorption and enhancement effects. These effects, which are matrix-dependent, are most often corrected by either empirical coefficients or by fundamental parameter calibration methods.

Empirical coefficients are derived after several calibration standards have been analyzed. These standards can be made from well-characterized site-specific materials or by treating clean materials with known quantities of analytes or both. This form of calibration requires the use of several standards bracketing the analyte concentration range of interest. For example, Table 2 shows that 18 standards were necessary for the analysis of a soil containing five metals over a range of 0 to 10,000 $\mu\text{g/g}$ (Piorek and Rhodes 1988). The preparation and verification of these standards could delay the start of an investigation by as much as a week or more, particularly when contaminated site-specific materials are involved, because they must be confirmed by alternative methods of total analysis. Furthermore, if site-typical soil standards are used, attention should be paid to the sand, clay, calcium and iron content (Piorek and Rhodes 1988). Thus, several sets of calibration standards, one for

Table 2. Set of calibration standards for the analysis of metals in soil.

| No. | Concentration ($\mu\text{g/g}$) | | | | |
|-----|-----------------------------------|------|------|------|------|
| | Cr | Cu | Zn | As | Pb |
| 1 | 0 | 0 | 0 | 0 | 4960 |
| 2 | 0 | 0 | 0 | 4957 | 0 |
| 3 | 0 | 0 | 4611 | 0 | 0 |
| 4 | 0 | 4907 | 0 | 0 | 0 |
| 5 | 3304 | 0 | 0 | 0 | 0 |
| 6 | 6251 | 6091 | 3517 | 2811 | 937 |
| 7 | 322 | 241 | 998 | 9656 | 3862 |
| 8 | 1965 | 1964 | 922 | 491 | 122 |
| 9 | 81 | 488 | 458 | 977 | 2929 |
| 10 | 2423 | 9080 | 8520 | 6356 | 1816 |
| 11 | 1265 | 949 | 6230 | 3794 | 6640 |
| 12 | 4530 | 3881 | 228 | 243 | 485 |
| 13 | 161 | 2898 | 1813 | 120 | 9660 |
| 14 | 0 | 0 | 0 | 0 | 0 |
| 15 | 0 | 2916 | 4560 | 0 | 0 |
| 16 | 0 | 4857 | 2734 | 0 | 0 |
| 17 | 0 | 0 | 0 | 4934 | 2960 |
| 18 | 0 | 0 | 0 | 2961 | 4935 |

each specific soil type, may be necessary for a single site.

Fundamental parameter analysis is based on physical constants (i.e. mass absorption coefficients, jump ratios and fluorescence yields), which eliminates the need for several calibration standards (Figura 1987, 1993). However, as with empirical calibration methods, the best accuracy is obtained when the reference standard has a particle size and matrix density similar to the samples being analyzed. This requirement may also impede investigations, since very few commercial reference materials are now available. Moreover, the multiple-variable approach of analysis used by both fundamental and empirical calibration methods rely on commercial software development and microprocessing, which leaves the analyst with a black-box approach to environmental sample analysis.

The analysis method used in this study for Cu, Zn, As and Pb relies completely on the measurement of the intensity of the K_{α} , K_{β} , L_{α} or L_{β} spectral line for a specific element, along with the Compton K_{α} backscatter peak (Fig. 3). This method of analysis allows for the determination of metal concentrations in environmental samples of similar physical state (particles $<600\ \mu\text{m}$) to be performed once element-specific response factors have been established using a certified reference material. For this study a finely ground soil, SRM 2710 certified

reference soil from the National Institute of Science and Technology (NIST), was used to establish the analyte response factors. The peak counts (intensities) used to establish the response factors for Cu, Zn, As and Pb are shown in Table 3. Even with a high-resolution XRF instrument, the As K_{α} and Pb L_{α} lines (10.532 and 10.549 keV, respectively) overlap, so the As K_{β} and Pb L_{β} peaks were used.

To perform this method of analysis with the 920 X-Met system, the energy spectrum from each analysis was saved and transformed into a 256-channel spectrum for close examination. This also

Table 3. Response factor determinations for Cu, Zn, As and Pb based on the SRM 2710 certified reference material.

| | Cu | Zn | As | Pb |
|--|------|------|-------|------|
| Response factor (intensity/concentration) | | | | |
| Day 1 | 12.0 | 33.9 | 1.09 | 39.5 |
| Day 2 | 11.9 | 34.8 | 0.90 | 38.0 |
| Day 3 | 12.3 | 34.4 | 1.04 | 39.6 |
| Average | 12.1 | 34.4 | 1.01 | 39.0 |
| Std. dev. | 0.21 | 0.45 | 0.098 | 0.90 |
| % RSD | 1.7 | 1.3 | 9.7 | 2.3 |
| SRM 2710 concentration ($\mu\text{g/g}$) | | | | |
| | 2950 | 6957 | 626 | 5532 |

could have been done by measuring the intensities from the original 2048-channel spectrum. The former approach was used because it is easier to measure the intensity (counts) of smoothed peaks, and once transformed, six spectra could be displayed simultaneously. Intensities of both the baseline and the peaks of interest were then measured by selecting the appropriate spectrum channels. This was accomplished by placing a cursor on the selected channel (keV) and recording the counts (intensity) off of the display. Concentration estimates were manually determined by multiplying the baseline-corrected analyte signal intensity by the normalization factor, then by the response factor. The normalization factor is the product of the Compton K_{α} peak intensity for the certified reference material divided by that of the samples.

METHOD EVALUATION

Detection limit

The sensitivity of this instrument for the determination of Cr, Cu, Zn, As and Pb in soil was evaluated for an empirical coefficient calibration and for the manual interpretation of peak intensities. Both procedures used the method detection limit (MDL) (Federal Register 1984), and analyses were performed using the set of generic soil standards shown in Table 2. The MDL establishes detection limits based on the standard deviation of replicate measurements multiplied by the appropriate t value (one-sided) for $n-1$ degrees of freedom at the 99% confidence level. Table 4 shows the results for the seven analyses of an individual sample after calibrating the instrument over a high (10000- to 0- $\mu\text{g/g}$) and low (1000- to 0- $\mu\text{g/g}$) concentration range. The soil standards chosen for repeated analysis had reported analyte concentrations of approximately 1000 $\mu\text{g/g}$ for the high calibration range and between 100 and 300 $\mu\text{g/g}$ for the low range. Between each analysis the sample was removed from the detector and shaken. All analyses were performed for a 120-second measurement period.

Analysis of reference and treated material

Several materials with either fortified or certified metal concentrations were used to assess the performance of the response factor/Compton K_{α} peak normalization analysis method. Table 5 lists the certified reference materials purchased from either NIST or the Resource Technology Corporation (RTC). Those purchased from NIST have cer-

Table 4. Method detection limits (MDLs) established for metals in soil and precision of analysis for samples with concentrations near 1000 $\mu\text{g/g}$.

a. Method detection levels ($\mu\text{g/g}$)

| Metal | Empirical calibration | | Peak intensity (counts) |
|-------|-----------------------|--------|-------------------------|
| | 10000-0 | 1000-0 | |
| Cr | 170 | 260 | 270 |
| Cu | 96 | 59 | 54 |
| Zn | 84 | 100 | 90 |
| As* | 49 | 42 | 41 |
| Pb† | 57 | 28 | 48 |

b. Precision and accuracy of empirical calibration analysis

| Metal | Accepted | Found | %RSD |
|-------|----------|-----------------|------|
| Cr | 1265 | 1270 \pm 53** | 4.2 |
| Cu | 949 | 872 \pm 31 | 3.6 |
| Zn | 922 | 899 \pm 27 | 3.0 |
| As | 491 | 500 \pm 16 | 3.2 |
| Pb | 937 | 924 \pm 18 | 1.9 |

* As-K β .

† Pb-L β .

** Average and standard deviation of seven analyses.

tified concentrations for the total amount of metal present, whereas the RTC materials report certified values based on the USEPA SW846, 3000-series metal acid extraction procedures (U.S. EPA 1986). All of these materials were air dried and have an average particle size of <600 μm . Analysis was performed after placing 4- to 5-g quantities in a 31-mm-diameter analysis cup with a 0.2-mil polypropylene X-ray film window.

In addition to the certified reference materials, six different soils were spiked with Cr, Cu, Zn, As

Table 5. Certified reference materials used in the test.

| | |
|--|--|
| National Institute of Standards and Technology | |
| SRM1579a—Powdered Lead Based Paint | |
| SRM2704—Buffalo River Sediment | |
| SRM2709—San Joaquin Soil | |
| SRM2710—Montana Soil | |
| SRM2711—Montana Soil | |
| Resource Technology Corporation | |
| CRM012—Incinerated Sludge | |
| CRM013—Paint Chips | |
| CRM014—Baghouse Dust | |
| CRM020—Soil (from USEPA Superfund site) | |
| CRM021—Soil (from contaminated waste site) | |

Table 6. Characteristics of the laboratory-treated soils.

| Matrix | % sand | % silt and clay | Grain size* (mm) | Weight† (g) |
|-----------------------------|--------|-----------------|---------------------|----------------|
| Ottawa sand | 100 | | 0.4 | 4 |
| Rocky Mountain Arsenal soil | NA | NA | NA | 1 |
| Lebanon Landfill soil | 45 | 55 | 0.3 | 4 |
| CRREL soil | NA | NA | NA | 4 |
| Tampa Bay sediments | 95 | 5 | 0.2 | 4 |
| Ft. Edwards clay | 30 | 70 | 0.03 | 2 |

* 95% cut off.

† weight of soil subsample spiked.

NA—Not analyzed.

and Pb using aqueous atomic absorption standards (Spittler and Fender 1979). Some of the soil characteristics and the subsample weights treated are shown in Table 6. These soils were air dried and thoroughly mixed prior to subsampling. Prior to treatment of each soil, six subsamples were placed into inverted 31-mm-diameter analysis cups. All analyte spikes were made by pipetting between 0.4 and 0.025 mL of concentrated 10,000-mg/L aqueous pure element standards (AESAR/Alfa, Johnson Matthey) directly onto the soil subsamples. An analyte spiking sequence was used so that none of the soil subsamples were treated with the same concentration twice (Table 7). In all, six cups were prepared for each soil matrix, five of which were spiked, increasing the Cr, Cu, Zn, As and Pb concentration by 1000, 500, 250, 125 or 0 µg/g; one served as the matrix blank. The total volume of solution added to each of the subsamples was less than 0.2 mL/g. This small volume of liquid completely wetted the exposed surface of the soil subsamples, with the exception of the one that had 70% silt and clay.

Once treated, the uncovered samples were placed in an oven at 95°C for one hour. After heating, the partially dried soil subsamples were

stirred with a stainless steel spatula. This process broke up the water-soaked grains, exposing a greater surface area and starting the homogenization process. Then the subsamples were returned to the oven for an additional hour of drying. After this second heat treatment, they were more carefully stirred, breaking up any clumps of soil that formed due to wetting. When no clumps remained and the soil subsamples were well mixed, the bottom of the analysis cup was covered with a 0.2-mil polypropylene X-ray cell film.

An analysis time of 120 seconds was used for Cu, Zn and Pb in the commercial reference materials. Determination for the metals in the laboratory-prepared soils and for As in the commercial reference materials required 300 seconds. All of the values for Cu, Zn, As and Pb were established relative to the SRM 2710 standard by using the response factor/Compton K_{α} peak normalization method. Tables 8 and 9 show the measured Compton K_{α} peak intensity (counts), along with the metal concentrations determined for each sample. No values were reported for Cr because no standard reference material was available with a total certified concentration greater than the MDL (270 µg/g, Table 4).

Table 7. Treatment scheme for spiking soil subsamples with metals.

| Subsample | Cr | Cu | Zn | As | Pb |
|--------------|------|------|------|------|------|
| S1 | 1000 | 125 | 0 | 500 | 250 |
| S2 | 500 | 250 | 1000 | 0 | 125 |
| S3 | 250 | 0 | 125 | 1000 | 500 |
| S4 | 125 | 1000 | 500 | 250 | 0 |
| S5 | 0 | 500 | 250 | 125 | 1000 |
| Matrix blank | 0 | 0 | 0 | 0 | 0 |

Table 8. Analysis of commercial reference materials based on single standard and Compton K_{α} peak normalization.

| Standard | Metal concentrations ($\mu\text{g/g}$) | | | | Compton K_{α} (counts) |
|--|--|-----------------|--------------|------------------------|-------------------------------|
| | Cu | Zn | As | Pb | |
| SRM 1579a Powdered lead based paint | | | | 119,950* [160,000]† | 29.6 |
| SRM 2704 Buffalo River sediment | 99 [31] | 438 [302] | 23 [26] | 161 [130] | 118 |
| SRM 2709 San Joaquin soil | 35 [105] | 106 [91] | 18 ND | 19 [18] | 124 |
| SRM 2710 Montana soil | 2,950 std** | 6,952 std | 626 std | 5,532 std | 101 |
| SRM 2711 Montana soil | 114 [167] | 350 [343] | 105 [138] | 1,162 [1,100] | 121 |
| CRM 012 Incinerated sludge | 3015 [2,470] | 635 [342] | | 120 [114] | 56.4 |
| CRM 013 Paint chips | | | | 643 [460] | 315 |
| CRM 014 Baghouse dust | | | | 1,914 [2,080] | 193 |
| CRM 020 Soil from Superfund site | 753 [687] | 3021 [4,420] | 397 [429] | 5,195 [5,070] | 54.1 |
| CRM 021 Soil from cont. waste site | 5,086 [8,720] | 574 [549] | 28 ND | | 23.7 |

* Certified value.

† Values in brackets were established relative to the SRM 2710 after Compton peak normalization.

** Certified standard used for response factors.

RESULTS AND DISCUSSION

The results in Table 4 show that the MDLs established by empirical coefficient calibration or by manually measuring peak intensities from the transformed spectra fulfill the requirement of providing detection capabilities $<1000 \mu\text{g/g}$ for Cr, Cu, Zn, As and Pb. This table also shows that the percent relative standard deviations (%RSDs) for empirical coefficients analysis of analyte concentrations around $1000 \mu\text{g/g}$ were $<10\%$. Likewise the %RSDs for the response factors shown for Cu, Zn, As and Pb in Table 3 were below 10%.

The results shown in Tables 8 and 9 demonstrate the usefulness of the single standard and Compton K_{α} normalization approach to estimating Cu, Zn, As and Pb concentrations in a variety of solid particle matrices (i.e. dust, soil, paint chips

and sludge). The values determined for the certified reference materials (Table 8) only showed two determinations to be off by more than 50% for samples with certified concentrations above the established MDLs (Table 4). These determinations were for Cu both in the SRM 2704 and CRM 021 reference materials. The high Cu value for the CRM 021 reference material as established by the response factor/Compton K_{α} peak normalization method is not necessarily incorrect, since the certified value is based on an acid extraction that may not represent the total amount present. In general the values below the MDLs were also in good agreement with the certified concentrations. Similarly the concentrations determined for the spiked soils (Table 9), after removing the background values (the mean of the $0 \mu\text{g/g}$ standard and the blank soil matrix) when they were found to be

Table 9. Concentrations ($\mu\text{g/g}$) of Cu, Zn, As and Pb determined for spiked soil matrices.

| Material and spike | Metal concentrations ($\mu\text{g/g}$) | | | | Compton K_{α} (counts) |
|-----------------------------|--|------|-------|------|-------------------------------------|
| | Cu | Zn | As | Pb | |
| Ottawa sand | | | | | |
| 1000 ppm | 1010* | 1020 | 1420 | 911 | 157 |
| 500 ppm | 534* | 458 | 381 | 411 | 153 |
| 250 ppm | 264* | 224 | 324 | 182 | 154 |
| 125 ppm | 132* | 127 | 72 | 139 | 156 |
| 0 ppm | 69 | ND | ND | ND | 149 |
| Matrix | 64 | 18 | ND | 10 | 150 |
| Rocky Mountain Arsenal soil | | | | | |
| 1000 ppm | 897* | 1050 | 1450 | 960 | 125 |
| 500 ppm | 483* | 459 | 608 | 470 | 124 |
| 250 ppm | 209* | 245 | 304 | 211 | 123 |
| 125 ppm | 93* | 153 | 105 | 125 | 125 |
| 0 ppm | 76 | ND | 37 | ND | 123 |
| Matrix | 62 | 2 | 41 | 23 | 124 |
| Lebanon Landfill soil | | | | | |
| 1000ppm | 859* | 872 | 988 | 1192 | 122 |
| 500ppm | 373* | 469 | 536 | 423 | 119 |
| 250ppm | 195* | 224 | 305 | 264 | 119 |
| 125ppm | 94* | 140 | 78 | 135 | 119 |
| 0ppm | 99 | 2 | ND | ND | 118 |
| Matrix | 70 | 8 | ND | 24 | 124 |
| CRREL soil | | | | | |
| 1000 ppm | 787* | 870 | 782 | 1030 | 114 |
| 500 ppm | 461* | 541 | 635 | 597 | 112 |
| 250 ppm | 250* | 247 | 320 | 178 | 113 |
| 125 ppm | 69* | 152 | 26 | 130 | 114 |
| 0 ppm | 86 | 48 | 48 | ND | 114 |
| Matrix | 62 | 59 | ND | 18 | 115 |
| Tampa Bay sediments | | | | | |
| 1000ppm | 842* | 939 | 1350* | 936 | 144 |
| 500ppm | 513* | 486 | 560* | 526 | 145 |
| 250ppm | 250* | 218 | 200* | 219 | 143 |
| 125ppm | 103* | 159 | 73* | 124 | 145 |
| 0ppm | 60 | 11 | 220 | 7 | 142 |
| Matrix | 71 | ND | 249 | ND | 147 |
| Ft. Edwards clay | | | | | |
| 1000 ppm | 711* | 831 | 906 | 785 | 99.9 |
| 500 ppm | 289* | 454 | 491 | 344 | 99.1 |
| 250 ppm | 144* | 332 | 229 | 150 | 98.3 |
| 125 ppm | 142* | 171 | 104 | 108 | 99.7 |
| 0 ppm | 199 | 81 | ND | 19 | 98.1 |
| Matrix | 218 | 80 | ND | 4 | 98.3 |

* Average of 0 ppm and matrix subsamples subtracted.

greater than the MDL, were almost always within 50% of the expected values. This agreement between expected and determined concentrations occurred even though the normalization for matrix differences (the Compton K_{α} peak normalization) ranged from 4.26 to 0.321, a relative change of

more than 400%. Thus, it appears that, at least for the XRF analysis of these four metals, the majority of analyte sorption or enhancement due to the matrix can be accounted for by Compton K_{α} peak normalization.

Furthermore, since the estimated metal concen-

trations coincided with the treatment levels, this technique would be very useful for locating hot spots, even when dealing with concentrations well below 1000 µg/g. These findings support the concept that the initial screening performed for Cu, Zn, As and Pb does not require generic or matrix-matched standards or an instrument capable of performing fundamental parameter analysis.

These findings do not diminish the need for developing site-specific standards when attempting to obtain the greatest accuracy achievable with XRF analysis. Both empirical coefficients and fundamental parameter analysis are clearly capable of providing more than adequate results for screening applications. However, if soils of highly variable composition or other solid particle matrices are encountered during a site investigation, thereby precluding the use of a single set of matrix-matched standards, the Compton K_{α} peak normalization method should prove to be effective without compromising the overall RI/FS objective. Similar studies have been planned for the analysis of chromium, iron, cobalt, nickel, mercury, thallium, selenium, silver, barium, tin, antimony and cadmium.

CONCLUSION

Determinations of Cu, Zn, As and Pb in a variety of soil matrices and three other solid-waste particulate materials were often within 50% of the expected values using a single certified reference material to establish the instrumental response factors and Compton K_{α} peak normalization to account for matrix differences. This alternative approach to XRF metal analysis is very useful and timely when screening a variety of matrices during RI/FS activities.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, Attention: Office Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

| | | | | | |
|---|--|---|----------------------------------|--|--|
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE July 1994 | | 3. REPORT TYPE AND DATES COVERED | |
| 4. TITLE AND SUBTITLE Screening for Metals by X-Ray Fluorescence Spectrometry Using a Single Calibration Standard | | | | 5. FUNDING NUMBERS | |
| 6. AUTHOR(S) Alan D Hewitt | | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, N.H. 03755-1290 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER Special Report 94-20 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Environmental Center Aberdeen Proving Ground, Maryland | | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER SFIM-AEC-TS-CR-94061 | |
| 11. SUPPLEMENTARY NOTES | | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. Available from NTIS, Springfield, Virginia 22161 | | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) Analysis for copper, zinc, arsenic and lead was performed on a variety of solid particle matrices using a portable, high-resolution X-ray fluorescence (XRF) spectrometer. All quantitative determinations were based on an instrumental calibration method that uses a single certified reference material to establish elemental response factors and the Compton K α peak to normalize for matrix discrepancies. This simple approach to XRF analysis circumvents the need to acquire matrix-matched standards for either empirical coefficients or fundamental parameter methods of calibration. Preliminary results show that response factor/Compton K α peak normalization is a promising approach when screening for these metals in soils, dust, paint chips and incinerated sludge. | | | | | |
| 14. SUBJECT TERMS Field screening Metal analysis Particle matrixes Soils X-ray fluorescence | | | | 15. NUMBER OF PAGES 17 | |
| | | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED | 18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED | 19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED | 20. LIMITATION OF ABSTRACT UL | | |